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Description

This invention relates to thin film optical variable articles having substantial color shift with changing angle of incident light and a method of accomplishing the same.

It is well known that there are two principal sources of colors perceived from material objects. They are 1) selective wavelength absorption or scattering of light by the object and hence selective reflection or transmission of the visible spectrum and 2) wavelength-dependent interference or diffraction effects arising fro superposition of reflected/transmitted wave fronts from surfaces having ordered structures with dimensions in the realm of light wavelengths. Selective absorption arises basically from the chemical composition and the interaction of the incident light with the structure of the object on an atomic level. This can occur from the bulk chemical properties of the object itself or from the presence of colorants (dyes, pigments and other additives) in an otherwise transparent medium. Interference colors, on the other hand, are observed quite generally when light is reflected or transmitted by surfaces comprised of assemblies of essentially plane parallel, thin layers, single or multilayer, with thicknesses in the range of fractions of visible light wavelengths or from profiled surfaces of periodic structure with profile dimensions of the order of light wavelengths. Interference effects together with selective absorption can, of course, occur simultaneously in varying degree in the same object. It is also well known that selectively absorbing objects without attendant interference producing properties will quite generally display little, if any, variation in colored appearance with gradations in viewing angle, whereas surfaces comprised of thin films or gratings can display very marked shifts in colored appearance with change in angle, depending on the specific structure.

Interference colors in thin films arise from the superposition of light waves that have undergone multiple reflection and transmission within a structure consisting essentially of a series of plane parallel layers of different optical properties that are fractions of light wavelengths in thickness. The phase as well as the amplitude of the light waves in combination gives rise to wavelength dependent constructive and destructive interference effects to provide a selective filtering of incident light. The optical properties referred to are the refractive index values of the layers. For a homogeneous, isotropic, non-absorbing medium, the refractive index is a real number (usually denoted by the letter "n"). If the layer is metallic in nature or, if otherwise, it shows significant absorption properties with respect to the passage of light through the layer, then the refractive index is generally characterized by a complex number of the form $N=n-ik$, where k is the absorption coefficient.

It is also well known that a colored object has associated with it a spectral reflectance curve and, if it is to some degree transparent, a spectral transmittance curve as well. The colors related to those curves can be described completely and accurately in terms of combinations of three quantities known as tristimulus values X, Y and Z which are determined mathematically as integrals of the products of three distribution functions covering the visible spectrum from about 380 to 770 nanometers (i.e., blue, green and red primaries) with the reflectance or transmittance curve of an object and the energy distribution function of the light source. Though colors can be specified in terms of the X, Y, Z tristimulus values, the colors can also be characterized equivalently by the use of normalized values

$$x = X/(X + Y + Z) \text{ and } y = Y/(X + Y + Z)$$

together with the tristimulus Y value. The x,y values are known as chromaticity coordinates. As is well known to those skilled in the art of colorimetry, a very useful device known as the CIE diagram can be developed by considering the loci of x,y values in a two-dimensional plot that correspond to all real colors. This diagram is comprised of a horseshoe-shaped curve in the x,y plane enclosing the domain of all such chromaticity coordinates together with a set of contours that relate individual pairs of values to the qualitative aspects of color, namely, dominant wavelength and purity that are closely associated with the perceived attributes of hue and saturation. The tristimulus Y value, by its definition in terms of the photopic response function associated with the human eye, provides a measure of the third dimension of color, namely, luminance, which relates to the psychological attribute of brightness.

In United States Patent No. 3,858,977 there is disclosed optical interference authenticating means. This authenticating means is comprised of a substrate and a filter overlying and attached to the substrate. The filter is composed of an optical interference layer or series of layers having known characteristics of spectral transmittance, and reflectance, both varying with the angle of incidence of light on the filter. The substrate has at least a portion thereof adjacent to the filter which has the property to absorb at least some of the light transmitted through the filter. Maximum contrast is obtained where the substrate surface is black. The resultant color reflected by the substrate is essentially additive in its effects on the color reflected by the interference filter and hence in its effect on the overall reflected color. In general therefore, the effect is to dilute the color reflected by the filter seen by itself. The patent also discloses the use of a carrier in the form of a transparent or colored polyester film. This polyester film may be retained as a protective covering or alternatively can be removed after the filter has been attached to the substrate.

There is no disclosure of the use of this carrier for any optical effects and, in particular, to provide any effects on the color of the optical interference authenticating means. The carrier merely serves as a mechanical carrier or a protective covering. GB-A-2 054 195 discloses a colour-selective mirror suitable for head-up displays, including a high and a low pass filter. Colour shift for different viewing angles is not disclosed. Even if at two viewing angles light of a single wavelength is output, the viewer sees at different angles only black (no intensity).

This invention provides a thin film optically variable article for producing substantial colour shift in reflected light at different angles of viewing from a spectrum of incident light, comprising a structural element having first and second surfaces, a multilayer interference coating carried on one of said first and second surfaces and producing an inherent colour shift with angle, said interference coating being formed of at least one period of a metal layer and a dielectric layer together with a metal layer which is opaque and highly reflecting disposed on the opposite side of said period to said incident light, and an optically angle insensitive substractive colourant means external of the multilayer interference coating and disposed on the side of the multilayer interference coating facing said incident light to remove an unwanted colour from the reflected light, whereby said substractive colourant means in combination with the multilayer interference coating modifies the inherent colour shift produced by the multilayer interference coating to provide a discrete colour shift from one distinct colour to another distinct colour at two different angles of incidence and a substantially achromatic colour at another angle of incidence, said substracting colourant means being either incorporated in the structural element or in an optically thick superstrate having a minimum thickness of 1.5 m.

The said another angle of incidence may be intermediate to said two angles of incidence.

The said another angle may be between 0 and 45°.

In a further embodiment said another angle of incidence may be greater than said two angles of incidence.

In any of the above arrangements said one distinct color may be blue and said another distinct color may be red.

Alternatively said one distinct color may be green and said another distinct color may be orange.

In a still further arrangement said one distinct color may be gold and said another distinct color may be green.

In any of the preceding arrangements said structural element is opaque and said distinct colors are seen by reflection.

In any of the preceding arrangements said subtractive colorant means may be carried within the structural element.

Alternatively said subtractive colorant means may be carried externally of the structural element.

The following is a description of some preferred embodiments of the invention reference being made to the accompanying drawings in which:

Figure 1 is a cross sectional view of an article incorporating the present invention in reflection mode utilizing the combination of a colorant carrying superstrate and a multilayer interference coating.

Figure 2 is a cross sectional view of an article incorporating the combination of the present invention with a protective topcoat, the whole of which is mounted on the substrate.

Figure 3 is a cross sectional view of another article incorporating the combination of the present invention utilizing an embedded construction.

Figures 4A and 4B are cross sectional views of articles incorporating the combination of the present invention utilizing a hot stamp transfer construction or a die-cut transfer construction.

Figure 5 is a chromaticity diagram of theoretical blue-to-red color shift designs with and without colorant in the superstrate.

Figures 6A, 6B and 6C are graphs showing the computed reflectance curves of the blue-to-red designs of Fig. 6 for 0°, 45° and 70° incidence angles respectively.

Figure 7 is a graph showing the computed overall transmittance of the (isolated) colorant carrying superstrate associated with the blue-to-red color shift design.

Figure 8 is the chromaticity diagram for theoretical green-to-orange color shift designs, with and without colorant in the superstrate.

Figure 9 is a graph showing the computed overall transmittance of the (isolated) colorant carrying superstrate associated with the green-to-orange color shift design of Figure 8.

Figure 10 is a chromaticity diagram for theoretical gold-to-green color shift designs, with and without colorant in the superstrate.

Figure 11 is a graph showing the computed overall transmittance of the isolated colorant carrying superstrate associated with the gold-to-green color shift design.

The optical variable article having an enhanced color shift with angle consists of a structural element carrying subtractive colorant means and having first and second surfaces. A multilayer interference coating is carried on one of these surfaces. The subtractive colorant means serves to modify the color shift with angle properties of the interference coating.

The color shift with angle properties of a given multilayer interference coating are inherent in the design; and most often they entail the undesirable characteristics for optical variable article applications of having rather high purity colors intermediate to and

beyond those at 0° and some other desired angle of incidence, say 45°. The reasons for the intermediate and steep angle colors are related to the generally encountered more or less continuous shift to shorter wavelengths of the spectral profiles of these filters with increasing incidence angle wherein there is only moderate attendant change in basic profile (averaged with respect to perpendicular and parallel polarization) so that, for example, in a reflection mode device, continuously varying portions of the spectrum are being strongly reflected. In the present invention, the reflected color shift properties of the multilayer interference coating are modified by the optical properties of a superstrate which is positioned on the side of the multilayer intereference coating that faces the incident light. The superstrate itself can be colored or carry a thin colored layer and thereby serves on subtractive colorant means. This concept involves incorporating selectively absorbing materials (absorbing or subtractive colorants) in the otherwise substantially transparent superstrate. This imposes an angle-insensitive filtering action upon the angle-sensitive properties of the multilayer interference coating lying beneath the subtractive colorant means. As set forth hereinafter, the combined filtering provided by the superstrate and the multilayer interference coating can markedly alter the color shift properties of the optical interference filter. Such a combination in addition to providing modified color shift with angle properties makes duplication of the combination as, for example, by counterfeiters substantially more difficult.

More particularly as shown in Figure 1, the thin film optical variable article 11 consists of an element 12 which is substantially transparent. It is provided with first and second surfaces 14 and 16. A multilayer interference coating 17 is carried on one of the surfaces and is shown in Figure 1 on the surface 14. Since the article 11 is being viewed in reflection from the side of the element 12, the element 12 can be called a superstrate because the superstrate 12 is on the side of the interference coating 17 facing the incident light. The viewer is indicated by the eye 18 which views a reflected ray 19.

In accordance with the present invention, the structural element 12 carries a dye or other form of colorant so that it serves as subtractive colorant means. The element 12 typically can be any conventional substantially transparent material such as glass, plastic and the like. The colorant can be incorporated in the material forming the structural element 12 or, alternatively, it can be incorporated into an optically thick layer on the superstrate. In order to be optically thick, such a layer must have a thickness in the range from about 1.5 to 2.0 µm (microns) at a minimum.

With reference to Figure 1, the optical system in reflection consists of an interference filter with angle-of-incidence-varying as well as wavelength-varying reflectance R_F coupled with a superposed substantially transparent, optically-thick, subtractive colorant carrying stratum (i.e. coloured superstrate) characterized by a rather low surface reflectance R_s and an internal transmittance factor $e^{-\alpha_s(\lambda)}$. The overall reflectance for this system is given by:

$$R = R_s + \frac{(1 - R_s)^2 R_F e^{-2\alpha_s}}{1 - R_F R_s e^{-2\alpha_s}}$$

R_s is essentially independent of wavelength and (considering the average value for perpendicular and parallel polarized light) is also nearly constant with varying incidence angle until quite steep angles are reached. The quantity $e^{-\alpha_s}$ does change with increasing incidence angle, but not in basic wavelength profile, since the variation is equivalent to an increase in colorant concentration. For angles up to and around 45°, the overall effect is not very significant, however, and thus it can be said that the superstrate is basically angle-insensitive in its optical properties.

Since R_s is assumed to be a rather small value, it follows that the dominant behavior of the overall reflectance can be described by the simple expression:

$$R \approx R_F e^{-2\alpha_s}$$

The prime contribution to the overall R is thus the product of the interference filter reflectance by the absorption factor of the subtractive colorant means. The effect of the colorant then is primarily subtractive with regard to the observed color from the filter by itself, and this effect can be rather dramatic at any given angle of incidence, primarily in blocking unwanted spectral components of the reflected color.

In Figure 2 there is shown a more specific embodiment of an article 31 incorporating the present invention which is provided with a protective coat and the whole of which is mounted upon a substrate which serves as a base. The overall combination consists of a substrate 32 which serves as a base. The substrate 32 can be formed of many different types of materials such as paper, glass, cloth, sheet plastic, leather and the like. It is provided with a surface 33 which carries the combination 34 of the present invention which is secured by an adhesive layer 36. The combination 34 consists of structural element 37 in the form of a dyed superstrate providing subtractive colorant means and a multilayer interference coating 38 underlying the structural element 37 and facing the adhesive layer 36. As explained previously, the structural elements 37 serving as a superstrate must be optically thick. It must therefore have a minimum thickness in the range of about 1.5 to 2.0 microns. If desired, a protective coat 39 can be provided which is carried by the combination 34. The protective coat is formed of a suitable material such as a transparent plastic to provide increased durability as, for example, scratch protection as well as chemical protection. In order to ensure that there is adequate adhesion be-

tween the substrate 32 and the coating 38, the surface of the substrate 32 can be prepared by adding a base coat (not shown). For example, for use with a porous substrate such as paper or cloth, the base coat can be a polymer which can be applied to the substrate and will fill in the interstitial passages in the substrate. This base coat can be applied by a printing process or alternatively by a hot stamp transfer process.

In Figure 3, there is shown another article incorporating the present invention in which the combination 43 of the present invention is embedded in the article. Thus as shown, the article which can be in the form of a sheet of paper or other material 42 has the combination 43 embedded therein. The combination 43 consists of a structural element in the form of a dyed superstrate 44 of the type hereinbefore described which is provided with surfaces 46 and 47 and in which the surface 46 carries a multilayer interference coating 48 of the type hereinbefore and hereinafter described. Thus it can be seen that the combination which can be any suitable size, for example, from 0.3175×10^{-3} metres or smaller in lateral dimensions to a much larger size and of any desired configuration as, for example, a circular shape, can be embedded in the sheet 42 during the time the latter is being made.

In Figure 4A there is shown another embodiment of an article incorporating the present invention which can be utilized in connection with hot die stamp transfers. As shown therein, the article 51 consists of a flexible carrier sheet 52 which is made of a suitable polymer film such as polyethylene terephthalate (PET) having a surface 53. A combination layered structure 54 incorporating the present invention is carried by the sheet 52 and is secured thereto in a suitable manner such as by a release coat 56 of a conventional type. The combination 54 consists of an element 57 of the type hereinbefore described which is provided with a surface 58. The element 57 is in the form of a substantially transparent, optically thick subtractive, colorant carrying polymer hardcoat. An adhesive layer 61 is provided over the interference coating 59 and is provided with a surface which is non-tacky at room temperature. The product as thus far described can be considered to be a hot stamp transfer foil which can be shipped and subsequently used. This hot stamp transfer foil can be utilized in conjunction with conventional equipment to advance the foil in such a manner so that the adhesive surface 62 faces the substrate and then using a combination of heat and pressure utilizing a die of a given pattern, the adhesive layer 61 will be bonded to the substrate as, for example, a substrate such as substrate 32 in Figure 2 in those areas delineated by the die pattern. After this transfer has been made, the carrier sheet 52 can be separated from the combination 54. After the transfer has been made, the carrier sheet 52 with the release coat thereon can be discarded. The final product will take the form shown in Figure 2 with the exception that the protective coat 39 would not be present. With an article such as shown in Figure 4A very little thickness is added to a substrate such as the substrate 32 in Figure 2 because the article as formed in Figure 4A can be relatively thin. For example, the total thickness of the article as shown in Figure 4A can be on the order of a small fraction of a mil.

In Figure 4B there is shown an alternate embodiment of an article incorporating the present invention which can be utilized in die-cutting operations. It differs from the embodiment shown in Figure 4A in that the adhesive 64 is different from the adhesive 61 used in Figure 4A. Typically it can be a conventional pressure sensitive adhesive which is deposited upon the interference coating 59. A release liner 66 is secured to the adhesive 64 for protecting the adhesive until the article is used. In the use of the product shown in Figure 4B, the pattern for the transferred article is defined by a die which cuts through the entire product as shown in Figure 4B. At the time of application of the product to a substrate, the release liner 66 is removed and then the article is pressed down onto the base substrate so that the adhesive layer 64 adheres to the substrate. In the construction shown in Figure 4, the release coat 56 may be eliminated if there is no desire to separate the polymer layer 52 from the structure 54 of the article. In such a situation, the combination 54 can be applied directly to the carrier layer 52.

In the embodiments of the invention shown in Figs. 1-4, two basic design configurations are utilized in constructing the multilayer interference coatings employed in the combinations. These two basic design configurations filter the spectrum into a sequence of high reflectance regions surrounded by low reflectance regions and thus lend themselves in principle to high purity color production. The detailed spectral characteristics of each of these two basic design types can be rather widely controlled by controlling the specific design parameters. One design type of the interference coating utilized in the present invention can be characterized as an all-dielectric system consisting of a periodic structure of alternating high and low index dielectric films. The other design type can be characterized as a metal-dielectric system and consists of a periodic structure of alternating metal and dielectric layers on a relatively high reflecting opaque metal layer. Clearly, the latter type can only be utilized in a reflection type optical variable article. The former if used in a reflection mode device will normally require a blackening treatment of the adjacent substrate surface to ensure optimum color producing effects.

The periodic structure of the alternating high and low index dielectric layers for an all-dielectric design can be written in the form

$$(\alpha L - \beta H)^q,$$

where α and β are units of quarterwave optical thickness of the low and high index materials (represented symbolically by L and H) at some designated wavelength λ_0 and q is the number of periods in the stack.

The metal dielectric design used in the present invention consists of a structure which can be written in the form

$$(M_1 - \alpha D)^q - M_2,$$

where M_1 and M_2 are the metal components (generally different), D represents a dielectric layer and α, q have the same meaning as in the expression for the dielectric design.

There are many variations which are obtainable within these two design frameworks by varying parameters, such as component index values, thickness ratios, number of periods, etc. Additionally, a number of variations and extensions of the designs can be obtained by using multicomponent periods, altering the period makeup to consider symmetrical periods, for example, of the form (α/2L-βH-α/2L) and also adding odd stack elements on either side of the periodic structure to modify reflectance behavior in the low reflectance regions, etc. These designs can be further modified by the judicious choice of the subtractive colorants used in the superstrate (or substrate in the case of a transmission mode device).

All of the variations in the thin film component have in common the basic characteristic of filtering the spectrum into a sequence of bands of wavelengths of comparatively high and low reflectance. Moreover, the resultant spectral profiles tend to shift with change of incidence angle of the light to produce changes of color with angle shift. In the description of the present invention, some additional comments relating to specific characteristics of the two basic designs are set forth below.

The theory of periodic all-dielectric stack behavior is well known. The particularly important performance aspect of the periodic all-dielectric stack in the present invention is the fact that such a stack exhibits high reflectance bands in certain spectral regions wherein the reflectance increases steadily towards 100% with increasing number of periods. This performance, along with other general performance features can be established mathematically by those skilled in the art. The other basic filter design type considered in the present invention, namely, the metal-dielectric stack, in its simplest form of a three-layer combination can be regarded as a Fabry-Perot reflection type interference filter. Such a design will be of the form M_1-αD-M_2, where M_2 is a highly reflecting, essentially opaque metal layer and M_1 is a rather thin metal film with high absorption properties. This design will show a sequence of high and low reflectance wavelength regions corresponding closely to the conditions that give rise to the nodes and antinodes of the standing wave electric field established by the reflector M_2. In the vicinity of an antinode wavelength position, where the electric field intensity is a maximum, induced absorption can be shown to occur in the thin metal layer M_1 resulting in a low reflectance. At a node position M_1 has little effect on the reflectance of M_2 and the overall reflectance remains high. The separations between the node and the antinode wavelength locations and thus between the low and high reflecting regions correspond to quaterwave optical thickness changes in the dielectric layer D. Ths basic reflectance profile for the three-layer metal-dielectric design as just described will be essentially retained in designs employing additional periods of (M_1-αD).

To obtain optimum performance in optical variable articles employing a metal-dielectric design, one would choose for M_2 the highest reflecting metal consistent with overall good durability properties, for D the lowest usable index material, and for M_1 a metal with high absorption properties. High potential absorption occurs for metals with a high nk product. Such generally is the case for the class of grey metals for which n is approximately equal to k.

Both the periodic all-dielectric designs and the metal-dielectric designs, as described above, have certain general features in common-especially the aforementioned feature of filtering the spectrum into a sequence of comparatively high and low reflectance regions. There are also significant points of contrast. Both types of design would tend to employ for the low index dielectric material the lowest index usable material in order to enhance the sensitivity to color shift with angle properties. Both types would also tend to employ higher-order interference (within a certain range) for the same purposes. An important contrast, however, is that for all-dielectric designs the reflectance in a given high reflectance band increases with the number of periods, as already stated, whereas for a metal-dielectric design the highest reflectance is achieved already with the simplest design, namely a three-layer coating.

Specific designs reflecting the concepts of the present invention will now be set forth. The discussion assumes in all cases the use of Illuminant C light source. A chromaticity diagram for a theoretical blue-to-red color shift optical variable article, employed in a reflection mode, using an all-dielectric multilayer interference filter design not claimed is shown in Fig. 5. The computed chromaticity trajectory is show plotted for angles of incidence ranging from 0° to 75°. The parameters for the all-dielectric stack in this example have been specifically chosen so as to produce in reflection a blue color at 0° and a shift towards a red color at 45°. The 0°, 45° and 75° incidence angle points are noted by asterisks on the trajectory for the two curves A and B. Curve A represents the chromaticity for the case of no colorant carried by the superstrate

and curve B represents the chromaticity for a subtractive colorant carrying superstrate. The curve B starts out with a high purity color as shown in Fig. 5 at 0°, in the 380 to 480 nanometer range and spirals into the achromatic or no color point at 75°. The design for the case of no colorant in the superstrate is set forth below:

$$[S] - [(4.172L)(0.963H)]^5 - [S']$$

(Design A in Fig. 5)

where S is the superstrate and S' is the substrate, where L is a low index material in quarter waves of a suitable type, such as magnesium flouride, and H is high index material in quarter waves of a suitable type, such as a mixed oxide of the type disclosed in U.S. Patent No. 3,034,924. The superstrate is formed of any suitable substantially transparent material, such as a glass or plastic. (The refractive index of the superstrate was assumed here to be 1.56, but may vary from 1.4 to 1.8.) It is desirable that the substrate exhibit no significant reflection. For this purpose the surface adjacent to the filter can be provided with a blackening agent or absorber. If there is significant reflection from the substrate, this will rather generally tend to dilute or water down the colors from the interference filter. The index of refraction of the substrate can be characterized by a complex number such as:

$$N_s' = 1.55 - i\ 0.005$$

where the imaginary part (0.005) is the absorption coefficient.

For a blue-to-red color shift article using an appropriate superstrate subtractive colorant the design is as follows:

$$[S^*] - [(4.219L)(0.974H)]^5 - [S']$$

(Design B in Fig. 5)

Here the index of refraction of the superstrate is a complex number of the form $N_s{*}= 1.56\text{-}i\delta$, where δ is a quantity that is dependent on the wavelength and characterizes the absorption or subtractive properties of the colorant.

The match point or design wavelength for both of the above designs is 550 nanometers.

In Figures 6A, 6B and 6C, there are shown computed reflectance curves over the range 380 to 770 nanometers for 0°, 45° and 70° of the above two designs with and without the colorant in the superstrate to illustrate the working principle of combining a selective absorber (subtractive colorant) with an angle sensitive multilayer interference filter. The broken line curves in the figures represent the design without colorant in the superstrate, whereas the solid line curves are for the design with colorant in the superstrate or carried by the superstrate. Figure 7 shows the computed overall transmittance of the colorant carrying superstrate by itself that is associated with this blue-to-red color shift design. It can be seen that the colorant utilized has a transmission band in the middle of the blue range at approximately 470 nanometers, then quite sharply cuts off most of the green spectral region centering around 550 nanometers and then becomes transparent again at longer wavelengths to allow a red reflection to come through.

When used in combination with an interference coating which has a blue spike, what is seen is the blue reflectance band along with a lower order reflectance band just beginning to come into the red region. When the object or article is tipped at 45° to the incident light, the properties of the colorant carrying superstrate do not shift substantially but the properties of the interference filter do shift. Now the incipient red reflectance band at 0° becomes more prominent in that it shifts into the visible range whereas the blue spike seen at normal incidence has now shifted close to the ultraviolet and becomes substantially blocked by the short wavelength cutoff of the subtractive colorant. Thus in the vicinity of 45°, a strong red reflection is being given. At an angle of 70° incidence, the reflectance band that was at 45° in the red has now shifted over into the green region at around 550 nanometers and is now effectively blocked out by the green absorption or subtraction in the colorant. If the colorant were not present, a vivid green color would otherwise be seen. By means of the blocking or subtraction action by the colorant, there is reduced reflectance and very little color at this latter angle. In going from the blue to the red, there is a region of transition which cannot be altogether avoided. Here the color goes essentially from a blue through a purple/magenta into a red. The use of the subtractive colorant will modify the transition to some extent, in this case primarily by enhancing the purity of the red. However, the subtractive colorant is very effective in reducing the steep angle colors that otherwise develop beyond 45° incidence.

In the blue to red design which is shown in Fig. 5 it can be seen that what is ideally desired is a "window" in the superstrate at about 470 nanometers wavelength that allows the blue reflectance peak of the filter at 0° incidence to come through and a second "window" at around 620 nanometers (both essentially stationary with varying incidence angle) that will pass the red reflectance peak that develops at around 45° incidence. The remainder of the visible spectrum should be absorbed or subtracted by the superstrate to cause a substantial change in the intermediate and steep angle properties of the optical variable articles arising from the multilayer filter component. In practice, by using currently available subtractive colorants for the superstrate in conjunction with a multilayer filter component, the purple/magenta intermediate colors are not substantially altered. The elimination or subtraction of the steep angle colors by the colorant, on the other hand. is verv dramatic.

Thus it can be seen that the combination of the

subtractive colorant carrying superstrate with the all-dielectric multilayer interference filter provides an effective blue-to-red color shift with angle device.

For the third dimension of color, namely, luminance, which is represented in this case by the luminous reflectance with respect to Illuminant C, the values at 0° and 45° are given for both the A and B designs in the chart appearing in Figure 5. Illuminant C is standard and well known to those skilled in the art.

Fig. 8 is a chromaticity diagram for a theoretical green-to-orange subtractive color shift device used in a reflection mode. The design for a superstrate without colorant is as follows:

$$[S] - [(4.626L)(1.067H)]^5 - [S']$$

(Design A in Fig. 8)

The design for a superstrate containing an appropriate subtractive colorant is set forth below:

$$[S^*] - [(4.566L)(1.054H)]^5 - [S']$$

(Design B in Fig. 8)

The materials and the indices of refraction are the same as for the design shown in Figure 5, i.e. an all-dielectric design not claimed, except that the $\delta(\lambda)$ values for the superstrate are different. The match point or design wavelength is at 550 nanometers. Again the 0°, 45° and 75° angle points are indicated by asterisks for the two designs. As can be seen from Figure 8. Curve B at 0° a strong green color is observed. The curve then passes through the achromatic or no color point at intermediate angles to a reddish orange color in the vicinity of 45°.

The luminous reflectance values for both designs at 0° and 45° are given in the table in the upper right hand corner of Figure 8.

The computed overall transmittance for the isolated subtractive colorant carrying superstrate associated with the green-to-orange color shift design is shown in Figure 9.

Fig. 10 is a chromaticity diagram for a gold-to-green color shift device used in a reflection mode. The design with a superstrate without colorant is as follows:

$$[S] - Pd_1 - 4.365L - Pd_2 - 4.365L - Pd(\text{opaque})$$

(Design A in Fig. 10)

where Pd is palladium and L is SiO_2 in quarterwaves. The physical thickness of the palladium layers is as follows:

$$d_{Pd_1} = 5 \text{ nanometers}$$

$$d_{Pd_2} = 10 \text{ nanometers}$$

The bottom palladium layer labelled "opaque" should be less than 0.1% transmitting and nominally over 1000 Angstroms in thickness.

The index of refraction of the superstrate is the same as in the foregoing examples.

Again the match point or design wavelength is 550 nanometers.

The design for a superstrate with an appropriate subtractive colorant is as follows:

$$[S^*] - Pd_1 - 4.46L - Pd_2 - 4.46L - Pd\ (\text{opaque})$$

(Design B in Fig. 10)

The other parameters for this design are the same as for the design without colorant in the superstrate. The $\delta(A)$ values for the superstrate S* again are different than in the foregoing examples. As can be seen from Curve B in Figure 10 at 0° at strong gold color is produced. At an intermediate angle a green color is produced and at a high angle of 75° the Curve B passes through the achromatic or no color point.

The luminous reflectance values for these designs are shown in the table in the upper right hand side of Figure 10.

The computed overall transmittance of the isolated colorant carrying superstrate associated with the gold-to-green color shift design is shown in Fig. 11.

From the foregoing it can be seen that three examples of color shift designs have been provided with each incorporating a colorant carrying superstrate to modify the reflected color shift with angle properties of the associated filter. Two of these designs ("blue-to-red") and ("green-to-orange") utilize all-dielectric filters helpful to explain the effect of the invention. The third design ("gold-to-green") uses a metal dielectric stack. In principle, all-dielectric and metal-dielectric designs according to the invention can be used more or less interchangeably tor a given color shift with angle design. The blue-to-red design shown in Figs. 5 and 6A, B, C and 7 utilizes a colorant carrying superstrate that incorporates a mixture of Rhodamine B (magenta dye) and Kyestone 3810 Thioflavine TCN (yellow dye). This combination is not necessarily an optimum colorant for a blue-to-red optical variable device or article due primarily to the presence of unwanted absorption in the blue spectral region. The combination does effectively cut off steep angle colors and also enhances the red purity around 45° incidence rather substantially. There is, however, a detectable loss of purity in the blue as well as a loss of reflectance at normal incidence. It should be appreciated there is always some loss of luminous reflectance from use of a colorant carrying superstrate. In many cases this is not important. However, in this case the loss at normal incidence is significant due to the low starting reflectance. The above noted dye combination is the best compromise using known materials.

The green-to-orange color shift design shown in Figure 8 and the gold-to-green design shown in Figure 10 use Solvent Yellow 42 dye in different concentrations.

The designs for the filters for each of these color shift types have been designated in the foregoing de-

scriptions. It will be noted that in each example the design construction is slightly different for the two cases of the superstrate with and without colorant. This was established so that the normal incidence dominant wavelength values would be equal for the two designs. As pointed out above, the chromaticity trajectory is plotted in every case over the range of incidence values from 0° to 75° as indicated by asterisks. Also as pointed out above, luminous reflectance values at 0° and 45° are provided to give data concerning this third dimension of the color.

The foregoing two classes of designs, the all-dielectric filters and the metal-dielectric filters have common features which make them applicable for use in optical variable articles. On theoretical grounds the all-dielectric filters would offer greater overall potential for design variability for use in optical variable articles provided no limit is placed on the number of layers used or the specific structure of the all-dielectric stack. However, some of this apparent theoretical advantage is lost by the spectral averaging effects involved in determining the color properties of any given design. From a practical point of view in producing reflection mode devices, moreover, a metal dielectric filter design according to the invention appears to be more practical for roll coating production because of the fewer layers required. Typically for a metal-dielectric filter, a layer structure as simple as three layers can be utilized and still provide very good optical variable article performance, since as already noted the highest ratio of maximum to minimum reflectance is already achievable with such a simple design. By contrast in order to establish high spectral purity along with reasonable luminous reflectance values in any practical all-dielectric stack design, a minimum of five layers and probably more may be required. The need for many layers tends to make such a design relatively impractical in any high volume coating production. Also, in optical variable article applications higher order interference is often necessary, and thus the use of substantial film thickness of individual layers can be required to obtain the best performance. This in turn can give rise to substantial mechanical stress within the coating with attendant durability problems, which has a greater tendency to arise with the use of increased numbers of layers in all-dielectric designs.

In the foregoing discussion, it has been tacitly assumed that all layer boundaries in films and superstrate or substrate were plane parallel and smooth, so that the reflecting and/or transmitting properties of the assemblies could be characterized as essentially specular in character. This was important in establishing the basic color shift with angle properties of the present invention. Clearly, a significant departure from specularity in a thin film optical variable article would seriously detract, if not destroy, its intended usefulness as herein described by introducing averaging effects that would tend to wash out the color effects normally seen. On the other hand, a certain degree of diffuseness of the reflected (transmitted) light may in some cases be desirable. If the diffuseness is suitably limited in extent, there is rather little loss in color purity, or in definition otherwise of the overall color shift with angle properties of the optical variable article, since in such cases light scattering is limited to narrow angle effects. Moreover, by this means a more pleasing appearance may be gained, reducing any "gaudiness" that might be associated with specular colors of high luminance and purity. Such diffuseness can be introduced rather effectively, for example, by the judicious choice of materials and/or processing used for the outermost optically thick layer of the device.

The present invention has many applications some of which may not be apparent at the present time. One particular application is its use as an anticounterfeiting device. Because of the difficulty of duplicating the optical properties of combinations of multilayer interference filters and colorant carrying superstrates or substrates, small portions or areas of the same can be incorporated in the labels of designer apparel, computer problems, video cassettes and any other type of article in which it is likely that counterfeiting may be attempted. In addition, the designs can be utilized for decorative purposes in costumes and scenery in theaters to create special effects. Other than having small areas of the optical variable article, it is possible to form a trademark or logo from the article of the present invention. For example, designer label clothes could have the name of the designer formed out of an article normally in sheet form as produced in a roll coating operation of the material of the present invention.

The present invention particularly lends itself to anticounterfeiting applications because duplication of the same would be very difficult and would require the application of very high technology to support a counterfeiting operation.

From the foregoing it can be seen that the optical variable article applications offer an exciting new technological area for exploitation of optical thin films. The interference coatings and the dyed substrates in combination possess a unique signature which cannot be copied without duplicating an essentially equivalent structure in the article, which as hereinbefore explained is difficult to do because of the very high technology which is involved. Duplication on color copying machines would be impossible, because the areas which carry the attributes of the present invention would copy as black or at most as an angle insensitive color.

Claims

1. A thin film optically variable article for producing

substantial colour shift in reflected light at different angles of viewing from a spectrum of incident light, comprising a structural element (12) having first and second surfaces (14,16), a multilayer interference coating (17) carried on one (14) of said first and second surfaces and producing an inherent colour shift with angle, said interference coating being formed of at least one period of a metal layer and a dielectric layer together with a metal layer which is opaque and highly reflecting disposed on the opposite side of said period to said incident light, and an optically angle insensitive subtractive colourant means (12) external of the multilayer interference coating and disposed on the side of the multilayer interference coating facing said incident light to remove an unwanted colour from the reflected light, whereby said subtractive colourant means in combination with the multilayer interference coating modifies the inherent colour shift produced by the multilayer interference coating to provide a discrete colour shift from one distinct colour to another distinct colour at two different angles of incidence and a substantially achromatic colour at another angle of incidence,said subtracting colourant means being either incorporated in the structural element or in an optically thick superstrate having a minimum thickness of 1.5 µm.

2. An article as claimed in Claim 1, characterised in that the metal layer of said period has a high absorption with a n/k ratio of near unity.

3. An article as claimed in Claim 1 or Claim 2, characterised in that said other angle of incidence is intermediate to said two angles of said incidence.

4. An article as claimed in any one of Claims 1 to 3, characterised in that said other angle of incidence is between 0 and 45°.

5. An article as claimed in Claim 2, characterised in that said other angle of incidence is greater than said two angles of incidence.

6. An article as claimed in any of the preceding Claims, characterised in that said one distinct colour is blue and said other distinct colour is red.

7. An article as claimed in any of Claims 1 to 5, characterised in that said one distinct colour is green and said other distinct colour is orange.

8. An article as claimed in any of Claims 1 to 5, characterised in that said one distinct colour is gold and said other distinct colour is green.

Patentansprüche

1. Mit veränderlichen optischen Eigenschaften versehener Dünnschichtgegenstand zur Erzeugung einer wesentlichen Farbverschiebung im reflektierten Licht bei verschiedenen Sichtwinkeln von einem Spektrum einfallenden Lichtes mit
   - einem Strukturelement (12), das eine erste und eine zweite Oberfläche (14, 16) hat,
   - einem mehrschichtigen Interferenzbelag (17), der auf einer (14) der beiden Oberflächen gelagert ist und eine inhärente, winkelabhängige Farbverschiebung hervorruft und der aufgebaut ist aus mindestens einer Periode einer Metallschicht und einer dielektrischen Schicht zusammen mit einer lichtundurchlässigen, hoch reflektierenden Metallschicht, die sich auf der dem einfallenden Licht abgewandten Seite der Periode befindet und
   - einem optisch nicht winkelsensitiven, subtraktiven Farbmittel (12), das sich außerhalb des mehrschichtigen Interferenzbelages befindet und auf der dem einfallenden Licht zugewandten Seite des mehrschichtigen Interferenzbelages angebracht ist, um eine unerwünschte Farbe aus dem reflektierten Licht zu entfernen, wobei das subtraktive Farbmittel in Kombination mit dem mehrschichtigen Interferenzbelag die vom mehrschichtigen Interferenzbelag erzeugte, inhärente Farbverschiebung modifiziert, um eine diskrete Farbverschiebung von einer bestimmten Farbe zu einer anderen bestimmten Farbe bei zwei unterschiedlichen Einfallswinkeln und eine im wesentlichen unbunte Farbe bei einem anderen Einfallswinkel zu erzeugen und das subtraktive Farbmittel enthalten ist entweder im Strukturelement oder in einer optisch dicken Überschicht mit einer minimalen Dicke von 1,5 µm.

2. Gegenstand nach Anspruch 1, dadurch gekennzeichnet, daß die Metallschicht der Periode eine hohe Absorption mit einem n/k-Verhältnis von nahe 1 hat.

3. Gegenstand nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß der andere Einfallswinkel zwischen den beiden Einfallswinkeln liegt.

4. Gegenstand nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß der andere Einfallswinkel zwischen 0 und 45° beträgt.

5. Gegenstand nach Anspruch 2, dadurch gekenn-

zeichnet, daß der andere Einfallswinkel größer ist als die beiden Einfallswinkel.

6. Gegenstand nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die eine bestimmte Farbe blau und die andere bestimmte Farbe rot ist.

7. Gegenstand nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die eine bestimmte Farbe grün und die andere bestimmte Farbe orange ist.

8. Gegenstand nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die eine bestimmte Farbe gold und die andere bestimmte Farbe grün ist.

Revendications

1. Article optiquement variable pour film mince, destiné à produire un déplacement notable de couleur dans la lumière réfléchie sous différents angles d'observation à partir d'un spectre de lumière incidente, comprenant un élément structural (12) ayant des première et seconde surfaces (14, 16), un revêtement d'interférence multicouche (17) porté sur l'une (14) des première et seconde surfaces en question et produisant un déplacement de couleur naturelle avec l'angle, ce revêtement d'interférence étant formé d'au moins une période d'une couche de métal et d'une couche diélectrique conjointement avec une couche de métal qui est opaque et hautement réfléchissante, disposée du côté de la période en question opposé à la lumière incidente, et un moyen colorant soustractif (12) optiquement insensible à l'angle, extérieur au revêtement d'interférence multicouche et disposé sur le côté du revêtement d'interférence multi-couche tourné vers la lumière incidente pour éliminer une couleur non désirée de la lumière réfléchie, de manière que le moyen colorant soustractif en association avec le revêtement d'interférence multicouche modifie le déplacement de couleur naturelle produit par le revêtement d'interférence multicouche afin d'engendrer un déplacement discret de couleur avec passage d'une couleur distincte à une autre couleur distincte sous deux angles d'incidence différents et une couleur principalement achromatique sous un autre angle d'incidence, le moyen colorant soustractif étant incorporé à l'élément structural ou à une couche supérieure optiquement épaisse ayant une épaisseur minimale de 1,5 µm.

2. Article suivant la revendication 1, caractérisé en ce que la couche de métal de la période en question a une forte absorption avec un rapport n/k proche de l'unité.

3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que l'autre angle d'incidence est intermédiaire entre les deux angles d'incidence en question.

4. Article suivant l'une quelconque des revendications 1 à 3, caractérisé en ce que l'autre angle d'incidence a une valeur comprise entre 0 et 45°.

5. Article suivant la revendication 2, caractérisé en ce que l'autre angle d'incidence est plus grand que les deux angles d'incidence en question.

6. Article suivant l'une quelconque des revendications précédentes, caractérisé en ce que l'une des couleurs distinctes est bleue et l'autre couleur distincte est rouge.

7. Article suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que l'une des couleurs distinctes est verte et l'autre couleur distincte est orangée.

8. Article suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que l'une des couleurs distinctes est or et l'autre couleur distincte est verte.

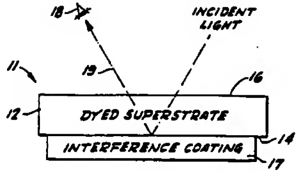
18
INCIDENT
LIGHT
11
19
16
12
DYED SUPERSTRATE
INTERFERENCE COATING
14
17

FIG_1

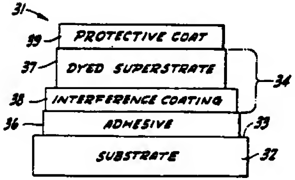
31
PROTECTIVE COAT
39
DYED SUPERSTRATE
37
INTERFERENCE COATING
38
34
ADHESIVE
36
33
SUBSTRATE
32

FIG_2

FIG. 3

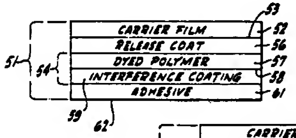

FIG. 4A

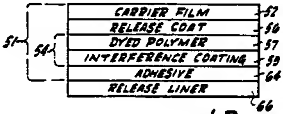

FIG. 4B

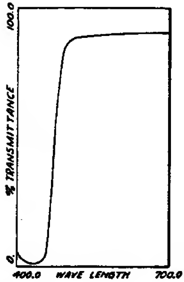

FIG. 11

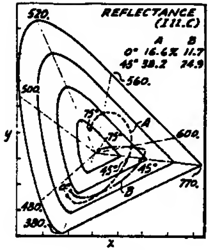

FIG-5

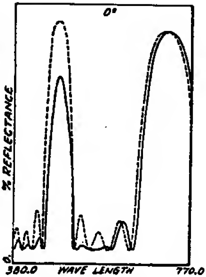

FIG-6A

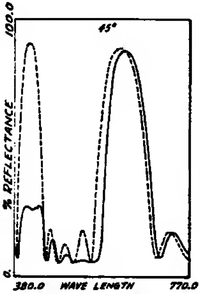

FIG-6B

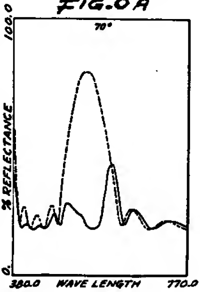

FIG-6C

FIG-7

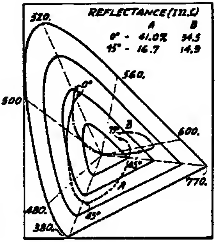

FIG-8

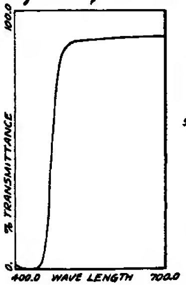

FIG-9

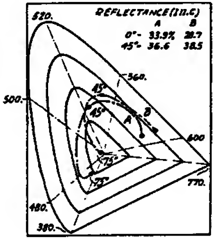

FIG-10